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BASALTIC AND GRANITIC ROCKS AS COMPONENTS OF CERAMIC MIXES FOR INTERIOR WALL TILES

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Basaltic and granitic rocks are studied as components of the raw-materials compositions for making ceramic tiles for interior walls. The combined introduction of granitic and basaltic materials increases the bending strength of tiles while preserving the physical-chemical properties required and improving sintering quality.

Key words: basaltic rocks, granitic rocks, melting temperature, clinopyroxene, ceramic tile, mechanical strength, structure, phase composition, thermal analysis, water absorption, shrinkage.

A promising direction of development of ceramic tile manufacturing is to reduce materials intensiveness, which is accomplished by decreasing tile thickness. The ceramic mixes used at enterprises in Belarus contain clay raw materials, granitic siftings, dolomite and quartz sand, which makes it impossible to obtain wares with reduced thickness without changing the process parameters because of inadequate strength of the intermediate and finished products. Basaltic rocks are widely used [1 – 2] for manufacturing wares to be used in construction, which are characterized by high strength, hardness and durability. In this connection the present study is devoted to a detailed analysis of the chemical-mineralogical composition and a comparative study of the technological properties of granitic and basaltic rocks as well as the physical-chemical properties of samples obtained from these rocks by means of ceramic technology using semi-dry pressing. The aim of the present work is to determine the efficacy of using basaltic rocks as a component in ceramic mixes for the manufacture of facing tiles with reduced materials intensiveness for interior walls.

Composite samples of granitic siftings from the Mikashevichskoe deposit (Belarus), basaltic rocks from the Rovenskoe deposit (Ukraine) and basaltic rocks surveyed on the territory of the Brest Oblast' in Belarus were studied.

Granitic siftings comprise the unconditioned run-of-mine fraction consisting of a mixture of granites, leucogranites, quartz diorites, diorites and other minerals combined under the general term granitic rocks. Siftings are an intermediate product with particle sizes 3 – 5 mm. When introduced into ceramic mix they play the role of a filling component and, as temperature increases in the annealing process, a partially fluxing component.

Basaltic rocks from Rovno Oblast', which are now being produced in Ukraine, find wide application in the production of mineral fibers and heat-insulating articles made from such, filament passing fittings obtained by thermoplastic molding and used in light-industry equipment and industrial textiles, stone casting for the needs of the mining industry and road stone [3 – 4].

Basaltic rocks of Vendian (neo-proterozoic) age surveyed on the territory of Belarus belong formally to traps of the Volynsko-Brest igneous province, which is widely disseminated on the southwest margins of the East-European platform, and lie at a relatively shallow depth (10 – 350 m) [5].

The chemical and mineralogical compositions of the experimental samples of granitic and basaltic rocks are presented in Tables 1 and 2 [5, 6]. The data in Table 1 attest an analogy of their qualitative chemical compositions of the samples; the quantitative content of oxides in the basaltic rocks fluctuates in a very narrow range (2 – 3%), which suggests that their compositions are identical.

The somewhat higher total content of alkali metal oxides, magnesium and iron in the basaltic rocks from Belarus could lower the melting temperature, while the elevated content of silicon and aluminum oxides in the granitic rocks as compared with basalts could increase their refractoriness.

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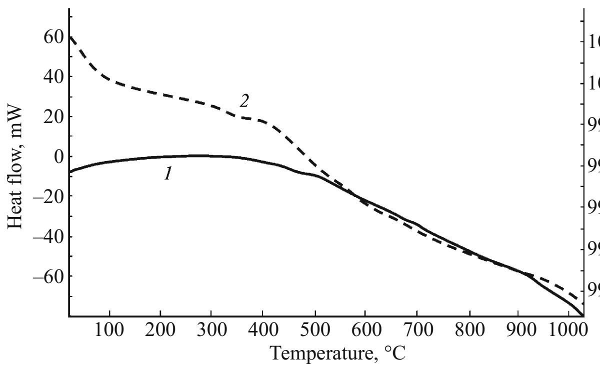

Fig. 1. Thermoanalytical curves of granitic rock: *1*) curve of the thermal changes occurring in the material; *2*) curve of the mass changes.

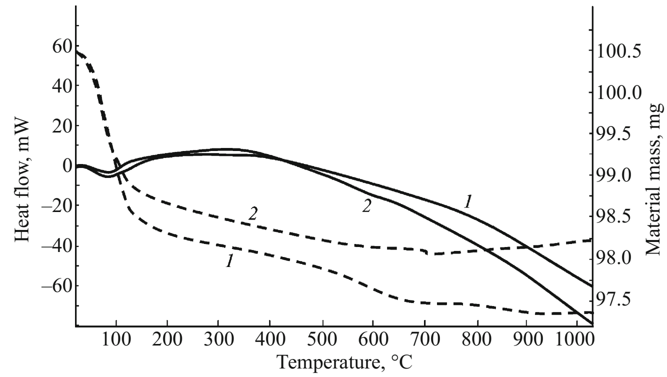

Fig. 2. Thermoanalytical curves of basaltic rock from Belarus (*1*) and Ukraine (*2*): ——) curve of the thermal changes occurring in material; – – –) curve of mass changes.

The data on the chemical composition of the rocks studied suggest that the introduction of basaltic rocks into the raw material mix will increase the amount of glassy phase somewhat during annealing of the ceramic mixes, which fills the pore space, increasing the density and therefore the mechanical strength of the material.

The data in Table 2 also attest an analogy of the mineralogical compositions of the basaltic rocks from Belarus and Ukraine. Due to the chain character of its structure clinopyroxene will strengthen the ceramic base while the content of the glassy components (chlorofeit and volcanic glass) will increase the amount of glassy phase during heat treatment.

The mineral composition of granitic rocks differs from that of basaltic rocks by the presence of quartz, biotite, amphibole and epidote; granitic rocks do not show chain minerals (pyroxenes) and glassy components (chlorofeit and volcanic glass). Secondary minerals can be represented by epidote and chlorite, occasionally by sericite and leucoxene. Magnetite, sphene, apatite, zircon and pyrite are the predominant auxiliary minerals [6]. In ceramic mixes basaltic rocks should play a role similar to that of granitic rocks.

The behavior of rocks on heating in the temperature interval 25 – 1000°C was studied by combined thermogravimetric analysis and differential scanning calorimetry using the TGA/DSC1 METTLER TOLEDO facility (Figs. 1 and 2).

It is evident from Fig. 1 that the curve of the thermal changes occurring in a material is characterized by the absence of thermal effects. The mass change curve corresponds

TABLE 1. Chemical Composition of the Experimental Rock Samples

Rock	Content, wt.%								
	SiO_2	Al_2O_3	CaO	MgO	K_2O	Na_2O	TiO_2	Fe_2O_3	P_2O_5
Basaltic, Maloritskii Rayon, Brest Oblast’	47.9 – 50.4	14.5 – 15.5	8.8 – 9.5	3.3 – 4.1	0.8 – 2.2	2.5 – 2.9	2.3 – 3.0	11.8 – 12.2	0.2 – 0.3
Basaltic, Vladimirskii Rayon, Rovno Oblast’	48.3 – 50.8	14.6 – 15.6	5.6 – 11.6	2.9 – 5.8	0.9 – 1.9	2.1 – 2.6	0.8 – 2.5	9.8 – 12.5	0.2 – 0.3
Granitic siftings from the Mikashevichskoe deposit	54.0 – 61.0	17.0 – 17.4	5.3 – 6.4	2.1 – 3.2	2.9 – 3.7	3.1 – 4.0	0.6 – 0.8	6.5 – 8.6	–

TABLE 2. Mineral Composition of Rocks

Rock	Mineral content, vol.%												
	Plagioclase	Quartz	Feldspar	Biotite	Amphibole	Epidote	Ore minerals	Chlorite	Olivine	Clinopyroxene	Chlorofeit	Volcanic glass	Analcite
Basaltic, Maloritskii Rayon, Brest Oblast’	40.0	–	1.0 – 3.0	–	–	–	8.0 – 10.0	–	3.0 – 5.0	35.0	5.0 – 10.0	1.0 – 2.0	1.0
Basaltic, Vladimirskii Rayon, Rovno Oblast’	45.0 – 55.0	–	–	–	–	–	8.0 – 10.0	–	–	20.0 – 30.0	8.0 – 20.0	1.0 – 1.5	0.5 – 1.0
Granitic siftings from the Mikashevichskoe deposit	50.0 – 60.0	7.0 – 12.0	1.0 – 5.0	10.0 – 20.0	5.0 – 15.0	4.0 – 7.0	–	1.0 – 3.0	–	–	–	–	–

TABLE 3. Physical-Chemical Properties of Basaltic and Granitic Rock Samples

Properties	Temperature, °C		
	1050	1100	1150
Granitic rocks			
Shrinkage, %	0.6	7.5	17.1
Density, kg/m^3	1794.3	2009.8	2302.0
Porosity, %	29.4	20.7	11.5
Water absorption, %	16.3	10.3	0.5
Bending strength, MPa	5.6	9.5	19.0
Basaltic rocks (Ukraine)			
Shrinkage, %	0.8	6.2	16.9
Density, kg/m^3	1935.7	2093.3	2445.0
Porosity, %	30.2	20.0	0
Water absorption, %	15.6	9.60	0
Bending strength, MPa	18.0	20.7	24.2
Basaltic (Belarus)			
Shrinkage, %	1.5	8.9	21.2
Density, kg/m^3	1950.0	2108.0	2678.0
Porosity, %	28.0	19.4	0
Water absorption, %	14.4	9.23	0
Bending strength, MPa	20.9	27.8	32.4

to evenly decreasing mass losses, comprising 1.3 mg associated with the removal of physically bound and constitutional water [7].

When Belarus and Ukraine basaltic rocks are heated their thermal-change curves are characterized by a single endo effect at 100°C, which corresponds to the removal of physically bound water. The mass-change curves show quite intense mass losses in the temperature interval 20 – 150°C followed by even descent on heating. The total mass losses are 2.25 mg for Belarus and 1.3 mg for Ukraine basalt.

To determine the melting temperature of rocks multicomposition heat-treatment of powdered samples in corundum crucibles in an electric furnace was performed at temperatures 1050, 1150, 1170, 1200, 1250 and 1300°C with 20 min soaking.

It was established that the melting onset temperatures are similar and equal to 1160 ± 5°C for Belarus and Ukraine basaltic and 1175 ± 5°C for granitic rocks. This is probably due to the difference of their chemical-mineral composition, specifically, the content of refractory silicon and aluminum oxides (see Table 1). The main changes in behavior are associated with the following processes: 1050 – 1150°C — compaction of sinter; 1160 – 1200°C — onset of melting, accompanied by the formation of a glassy phase; 1210 – 1300°C — complete melting with formation of viscous crystallized melt.

To study the physical-chemical properties of the rocks the experimental samples were comminuted, sieved with a No. 1 sieve to residue 3 – 5% and 60 × 20 × 6 mm bars were made by semi-dry pressing under specific pressure 25 MPa. In ceramic tile manufacturing the character and quality of sintering is determined in the temperature interval 1050 – 1150°C. For this reason the samples were fired at temperatures 1050, 1100 and 1150°C and then the properties were measured by the appropriate means (Table 3).

The data in Table 3 attest that as the heat-treatment temperature increases to 1150°C the water absorption of basaltic rock decreases to 0%, the mechanical strength increases and porosity decreases as a result of the presence of chlorofeit and volcanic glass, which promote the formation of an adequate amount of a cementing liquid phase, resulting in practically complete sintering.

Comparative studies of the physical-chemical properties of the basaltic and granitic rock samples showed that sintering produces a more uniform texture distinguished by high density and strength, which determines the elevated physical-chemical indicators. Replacing in part the granitic siftings in the initial compositions ceramic mixes by basalts should strengthen interior ceramic wall tiles and, correspondingly, increase the bending strength, which will contribute to the improvement of the technological process and decrease material intensiveness by decreasing thickness.

The production composition of ceramic mix used to make interior wall tiles by a single firing were taken for subsequent studies. An equivalent replacement of granitic by basaltic siftings in amounts 5 – 20 wt.% in steps 5% was made in the raw-material composition; the total content of both rocks remained constant. Laboratory samples of ceramic tiles were made by the following scheme: ceramic slurry preparation – water removal – molding powder preparation – semi-

TABLE 4. Compositions and Physical-Chemical Properties of Ceramic Tiles

Properties	Composition No.				
	1	2	3	4	5
Basalt content, %	0	5.0	10.0	15.0	20.0
Water absorption, %	14.5	12.8	12.0	11.5	8.3
Shrinkage, %	0.9 – 1.0	0.9 – 1.0	1.0 – 1.1	1.0 – 1.2	2.5 – 2.7
Post-sintering ultimate bending strength, MPa	28.0 – 29.0	32.0 – 33.0	34.0 – 34.5	35 – 36.5	36.0 – 37.5
CLTE, 10^{-6} K^{-1}	6.95	7.05	7.19	7.21	7.25

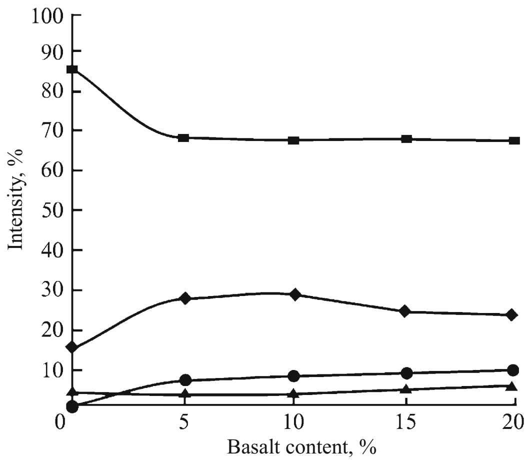

Fig. 3. Dependence of the intensity of the diffraction peaks of crystalline phases on the amount of basalt: ■) quartz; ◆) anortite; ●) augite; ▲) hematite.

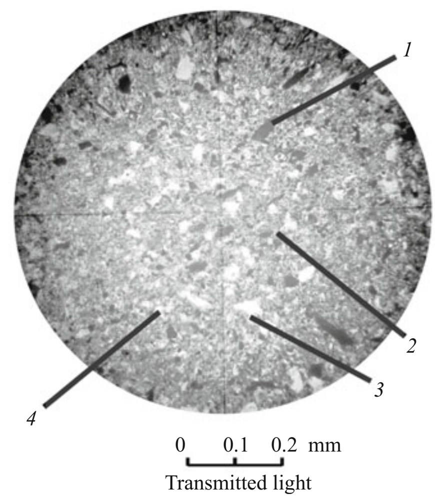

Fig. 5. Photograph of a thin section of a ceramic tile containing 15 wt.% basalts.

dry two-step pressing. The series of experimental samples with different content of basaltic were given the label KMB; their physical-chemical properties are presented in Table 4.

It was determined that as the amount of basaltic rock increase to15% the mechanical strength increases and the water absorption decreases. However, when 20% basaltic rock is introduced, together with a continuing increase of the mechanical strength shrinkage increases considerably to 3.2% as a result of an increase in the glassy phase amount during heat-treatment, which is a negative factor because tile dimensions vary.

In summary, a ceramic mix composition with 15% basalt was chosen as optimal on the basis of a complex of the physical-chemical properties which were studied.

X-ray phase analysis of the samples of ceramic tiles with basaltic rock substituted for granitic rock showed that when basalt is added to the raw-material composition a crystalline phase — augite Ca(Mg, Fe, Al)[(Si, Al)$_2$O$_6$], which is a chain clinopyroxene present in basaltic rock, is determined during heat-treatment together with anortite Ca[Si$_2$Al$_2$O$_8$], quartz SiO_2 and hematite Fe_2O_3. Probably, this is one reason for the higher bending strength in the sintered state due to reinforcement of the structure of the ceramic base of the facing tile.

To study phase formation in basalt-containing mix during sintering, the dependence of the intensity of the diffraction peaks of the crystalline phases presented above on the basalt content was studied; the results are presented in Fig. 3.

The studies showed that as the basalt amount increases the augite diffraction peaks increase in intensity; this is due to the increase in the content of this crystalline phase.

The microstructure of the sintered tile samples obtained from ceramic mix containing no basalt rock (composition 1) and 15% basalt (composition 4) was studied by scanning electron microscopy. The results are presented in Fig. 4.

An evaluation of the microstructure showed that as basalt is added the degree of crystallinity of the samples increases, the glass and crystalline phase are distributed more uniformly, and the structure is represented by crystals of different habitus fluctuating in the size range 10 – 100 μm.

The results of petrographic studies of the microstructure of a thin section of a tile sample with 15 wt.% basalt in the raw-material composition are presented in Fig. 5. They supplement the data from x-ray phase analysis and electron microscopy and show that the sample possesses a pelite-silt type structure. The content of clayey material is about 50%; the content of silt materials with sizes from 0.05 mm to 0.1 mm, represented by fragments of different minerals with

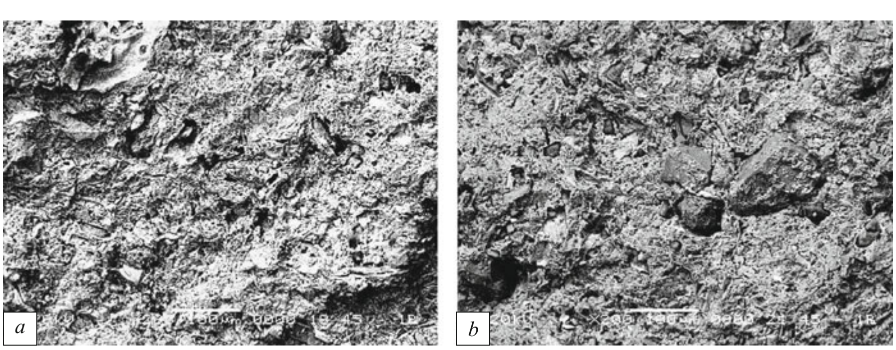

Fig. 4. Electron-microscopic image of a cleavage surface of ceramic tile samples: *a*) composition 1; *b*) composition 4 (see Table 4).

irregular shape (angular, often sharply angular) is: plagioclase — 10%; quartz — 15%; clinopyroxene — 5 – 7%; decomposed isotropic volcanomictic material to 15%, represented mainly by amorphous glassy matter with 0.05 mm to (0.3 × 0.1) mm crystalline fragments present in basalts, ranging in color from brown to brownish-yellow. The pore space comprises no more than 7 – 10%; the pores have an irregular configuration and are distributed chaotically with no visible regularity.

Thus, the samples of ceramic tile with composition 4 have a heterophase structure and are represented by crystalline, glassy and gas phases; a rational combination of these phases gives not only a dense uniform texture and microstructure of the sample but also high strength, together with the required water absorption, density, porosity and shrinkage.

In summary, a complex study of the chemical-mineralogical composition and technological and physical-chemical properties of basalts has shown that when used as raw-material components they can intensify sintering of the ceramic paste and, correspondingly, improve the quality of the final product.

The closeness of the compositions, the sameness of the behavior under heating and the indicators of the physical-chemical properties of Belarus and Ukraine basaltic rocks show that they can be used to make interior wall tile. Commercial development of this promising raw material in the Republic of Belarus could make it possible to eliminate mineral imports.

The simultaneous presence of granitic and basaltic raw materials in the compositions used to manufacture interior wall tiles is effective because this increases the bending strength considerably, which is one of the most important criteria for lowering materials intensiveness.

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